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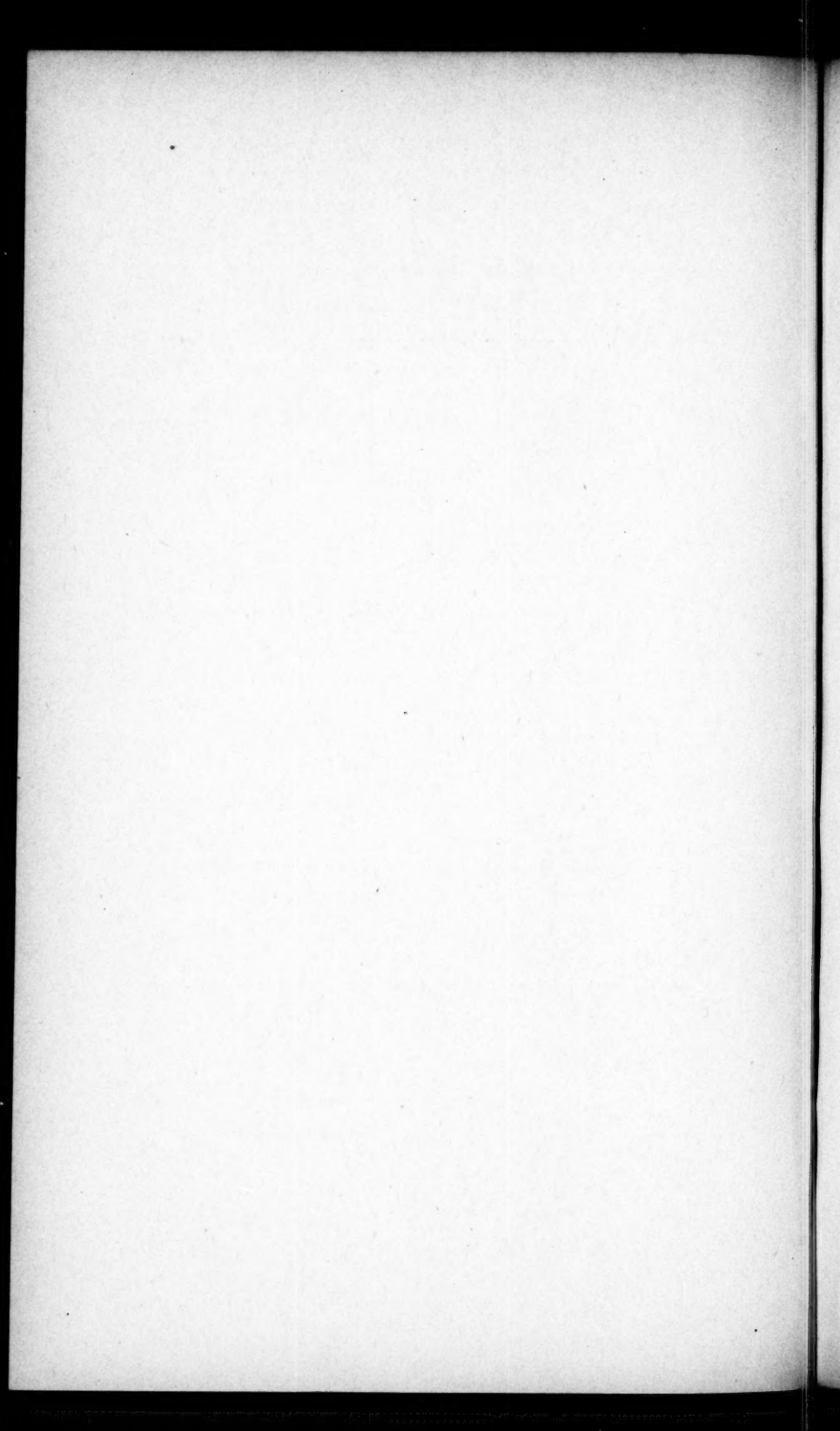
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LIV. — ON THE EQUILIBRIUM OF THE SYSTEM
CONSISTING OF CALCIUM CARBIDE, CALCIUM
CYANAMIDE, CARBON, AND NITROGEN.

BY M. DE KAY THOMPSON AND ROBERT H. LOMBARD.

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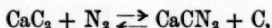
LIV. — ON THE EQUILIBRIUM OF THE SYSTEM CONSIST-
ING OF CALCIUM CARBIDE, CALCIUM CYANAMIDE,
CARBON, AND NITROGEN.

BY M. DE KAY THOMPSON AND ROBERT H. LOMBARD.¹

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1. INTRODUCTION.

SINCE the discovery by Frank and Caro² that pure nitrogen is absorbed by impure calcium carbide at high temperature, according to the reversible reaction :



calcium carbide has been employed on a commercial scale for the fixation of atmospheric nitrogen. This method yields four times as much nitrogen for a given amount of power as the direct oxidation in an electric arc. Calcium cyanamide can be used directly as a fertilizer, or it may be the starting point for the manufacture of other nitrogen compounds. In consequence of the importance of this reaction, we were led to undertake the determination of the equilibrium pressure of the nitrogen in the above reaction for a number of different temperatures. In this system there are three components, and four phases; consequently, according to the phase rule there will be one degree of freedom; or for every temperature, a corresponding pressure at which equilibrium will exist.

The method of carrying out this investigation was to heat a graphite crucible containing graphite, calcium carbide, and calcium cyanamide, in an Arsem vacuum furnace³ in an atmosphere of nitrogen. The

¹ The following research was carried out under a grant from the Rumford Fund of the American Academy of Arts and Sciences. Grateful acknowledgment is hereby made to the trustees of this fund.

² *Z. f. angew. Chem.*, **19**, 853 (1906).

³ *Trans. Am. Electroch. Soc.*, **9**, 163 (1906).

heating current was taken from a transformer in steps of 12 volts, and fine adjustment of the current was obtained by a carbon plate rheostat. The pressure was indicated by a mercury manometer, one arm of which was connected with the furnace; the other was evacuated and sealed off. The arrangement of the apparatus is shown in Figure 1. It was intended to measure the temperature of the crucible by means of a

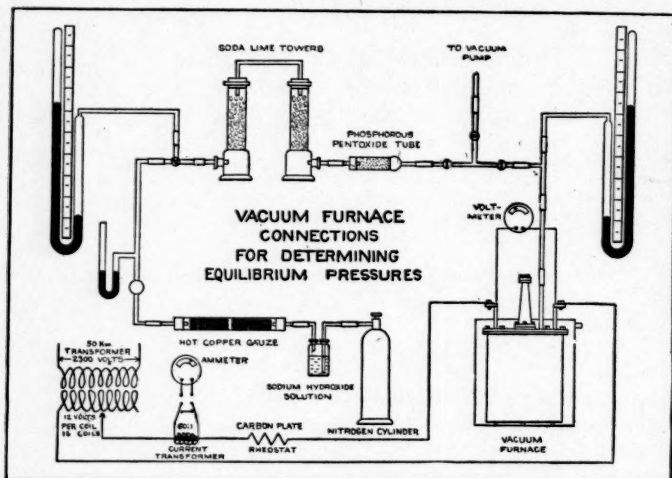


FIGURE 1.

thermo-electric junction entering the furnace through the tower projecting above the water in which the furnace was immersed, and two or three such runs were made. The wires of the couple were insulated from each other by different kinds of tubes. One wire was covered with a tube one millimeter in diameter, and this tube and the other wire were placed in a larger tube sealed at the end covering the junction. These tubes were long enough to reach up into the tower when their lower end was resting in the crucible. The hot end of the tube surrounding the wires of the thermo-electric couple was covered with a short graphite tube to protect it from the material in the crucible. No tubes that were available, however, would stand a temperature above 1200°C . Even Berlin porcelain was spoilt after a few hours' heating. Carbon seemed to have penetrated the whole mass of the porcelain where it was surrounded by the graphite spiral heater, and as much of

the couple as was heated was also spoilt. It was therefore necessary to give up the direct measurement by the thermo-couple and use a Wanner optical pyrometer. The instrument used in this investigation had just been calibrated by the Bureau of Standards, with results that were not materially different from the calibration furnished by the makers. The amyl acetate lamp was not sufficiently constant, however, and

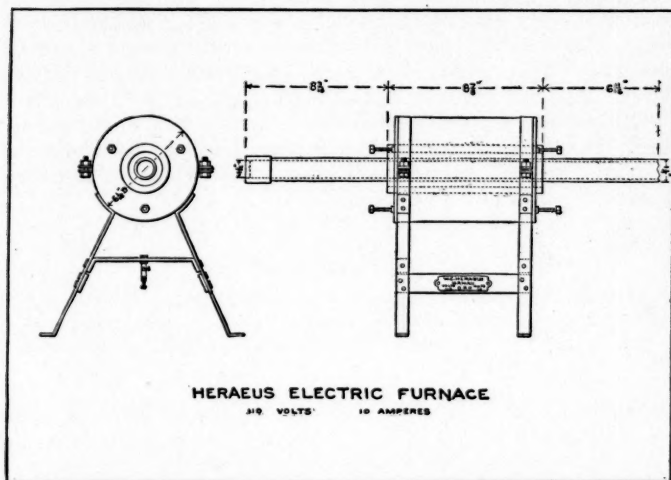


FIGURE 2.

therefore adjustment of the current in the small electric lamp of the Wanner pyrometer was made as follows: A furnace, shown in Figure 2, was made by wrapping platinum foil one fourth inch wide and 0.001 inch thick about a Royal Meissen porcelain tube of 2.54 centimeters inside diameter. A cylindrical piece of carbon was placed in the furnace, and a small porcelain tube was passed through the larger one and through a hole in the carbon. The smaller tube was to hold a thermo-electric couple, the junction of which was in the same plane as one of the faces of the carbon. The temperature of this face of the carbon was therefore given directly by the thermo-electric couple. In order to adjust the current in the Wanner pyrometer, the reading of the Wanner was set to agree with that of the couple, a piece of glass cut from the same plate as that closing the end of the tower of the vacuum furnace was placed in the groove in the pyrometer provided for holding the smoked

glass sometimes used for increasing the range of the instrument, and the pyrometer was sighted on the carbon. The current was then adjusted till the two fields in the pyrometer had the same appearance. The small furnace was kept heated during each run, and before measuring the temperature of the vacuum furnace a comparison was always made with the thermo-electric couple. It was found by this means that the current in the lamp as adjusted from day to day was much more constant than when the amyl acetate lamp was used as a standard, but it will be seen from the tables below that the current was not absolutely constant. This must have been due to a variation in the electric lamp itself. The following table shows the effect of a change of the current in the lamp on the apparent temperature as measured by the pyrometer. The temperature of the body measured was held constant in the vacuum furnace. The current is given in arbitrary units equal approximately to tenths of an ampere.

TABLE I.

Current in Wanner Pyrometer.	Temperature.
6.0	1304
6.1	1295
6.2	1282
6.3	1263
6.4	1263
6.5	1241
6.6	1226

The current could not be set better than to 0.1 of a unit, corresponding on the average to 10 degrees.

In order to see how the temperature varied in the auxiliary furnace, the temperature was taken with the junction by placing it at different distances from the carbon block, which was placed near the center of the tube. The results are given in Figure 3, which shows that no appreciable error would be introduced if the junction had not been exactly in the same plane as the surface of the carbon plate.

The calcium carbide used in the following experiments was all made at one time from Merck's lime and turnings from Acheson graphite electrodes. It was analyzed by the loss in weight method and found $78\frac{1}{2}$ per cent pure. It was ground up and passed through a sieve with 36 meshes to the linear inch before the analyses were made.

The method of carrying out the experiments was as follows: the crucible was filled nearly to the top with the carbide, was covered with

a graphite lid with a hole in it, and then placed in the furnace. The furnace was pumped out and the charge heated to a temperature at which the experiment was to be made (or higher) until all gases were driven off. Nitrogen, made by the Linde process and 90 per cent pure, was let into the furnace after passing it over hot copper, soda, lime, and phosphorous pentoxide. After allowing the nitrogen to enter the furnace until the pressure was 2 or 3 centimeters, it was pumped

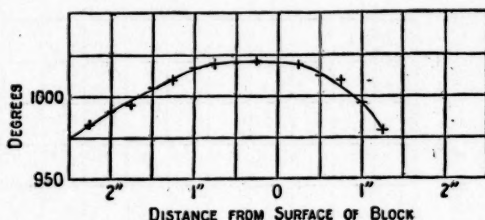


FIGURE 3. Temperature in Heraeus furnace at different distances from the surface of carbon block used for calibrating the Wanner pyrometer. The surface faced the pyrometer towards the left, in the figure.

out to about 1 or 2 millimeters. This was repeated once or twice to remove all other gases. The furnace was then filled with nitrogen to a pressure that was certainly greater than the equilibrium pressure. The furnace was usually hot when filled. The furnace was frequently filled in the afternoon and the run started the following morning. On heating with an excess of nitrogen some of it would be absorbed, producing calcium cyanamide and carbon from the carbide, so that all three solid phases were then present. After equilibrium had been reached from this side, nitrogen was pumped out, and the equilibrium was approached from the other side. The mean of the two results was taken as the best value of the equilibrium obtainable.

2. EXPERIMENTAL DATA.

A Siemens and Halske millivoltmeter of 471 ohms resistance was used for measuring the temperature with a platinum platinum-rhodium junction. The millivoltmeter was calibrated and the following table contains the corrected value of the scale reading with the corresponding temperature.

TABLE II.

CALIBRATION OF THERMO-ELECTRIC JUNCTION.

	Temperature Centi- grade of Melting Point.	Millivolts.	Log. of Temperature.	Log. of Millivolts.
Sulphur	447.7	3.56	2.6481	0.5515
Antimony	630.7	5.38	2.7998	0.7307
Aluminum	656.0	5.59	2.8169	0.7474
Copper	1083.0	10.19	3.0346	1.0081

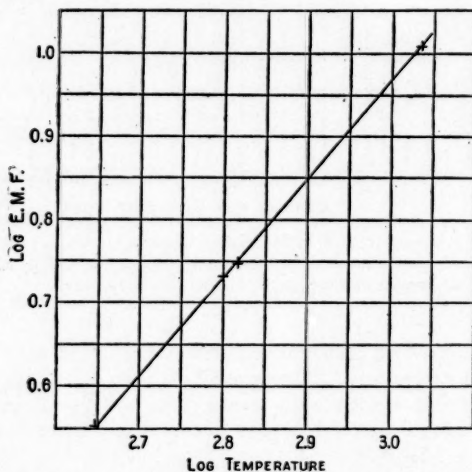


FIGURE 4. Calibration of thermo-electric couple.

The logarithms of the temperatures and pressures are seen from Figure 4 to lie on a straight line.

The pressures given in the following tables are in millimeters of mercury, and the temperatures in centigrade degrees. The numbers of the experiments are those recorded in the laboratory note-book. These tables contain only an abbreviated record of the experiments. Under the heading "Kilowatts" is given the product of current and amperes divided by 1000, not taking into account the power factor of the furnace.

Experiment 4.

The following experiment was carried out before the method of standardizing the Wanner pyrometer described above had been adopted.

Temperature measurements of the charge were therefore made with different values of the current in the lamp of the Wanner pyrometer, and the correct value, with its corresponding temperature, was determined subsequently from Table I.

	Time.	Kilowatts.	Pressure.
<i>Apr.</i> 28.	1.23 P. M.	8.36	317.8
	1.50 "	8.26	276.3

Some nitrogen was pumped out, in order not to use up all the carbide.

	1.52 P. M.	8.52	264.0
	4.45 "	8.52	267.4
<i>Apr.</i> 29.	12.35 "	8.52	267.8
	2.22 "	8.53	270.0

Here the pressure had become nearly constant, so nitrogen was admitted.

	2.25 P. M.	8.48	277.0
	4.45 "	8.52	273.3

The equilibrium pressure is therefore between 270 and 273, or 271.5 millimeters of mercury. The temperature, determined as explained above, was 1263° C.

Experiment 6.

A fresh charge of 33.7 grams of carbide was used in the following experiment.

	Time.	Kilowatts.	Pressure.
<i>May</i> 11.	2.55 P. M.	7.65	281.7
	4.05 "	7.66	224.0
	4.37 "	7.66	223.6

The pressure had become nearly constant, so nitrogen was admitted.

	4.45 P. M.	7.66	226.3
	5.10 "	7.66	225.1
<i>May</i> 12.	12.40 "	7.70	218.5
	1.00 "	7.00	222.7
	2.22 "	7.58	223.0

Nitrogen was again pumped out.

	2.23 P. M.	7.58	214.1
	4.30 "	7.52	224.7
<i>May</i> 13.	1.45 "	7.56	224.6
	2.45 "	7.61	223.5

The pressure had become nearly constant at 224 millimeters, so nitrogen was admitted.

Time.	Kilowatts.	Pressure.
2.55 P. M.	7.61	236.0
5.05 "	7.40	224.7

The mean temperature was 1223° , with the current in the lamp of the Wanner pyrometer 6.4 units. The equilibrium pressure was determined twice from each direction, and was found to be 224 millimeters.

Experiment 7.

The following experiment was made with the same charge as in 6.

	Time.	Kilowatts.	Pressure.
May 17.	2.35 P. M.	8.98	275.3
	3.45 "	8.98	282.9

The pressure was increasing very slowly, possibly all calcium cyanamide having been decomposed. Nitrogen was admitted.

	3.50 P. M.	8.98	316.5
	4.55 "	8.98	304.2
May 18.	1.30 "	8.92	305.6
	3.00 "	8.78	305.1

The pressure had become nearly constant. Nitrogen was therefore admitted.

	3.02 P. M.	8.78	329.2
	4.45 "	8.71	311.8
	5.00 "	8.71	313.0
May 19.	12.30 "	8.78	312.5
	1.13 "	8.71	312.9

The pressure was nearly constant. Some nitrogen was then pumped out.

	1.18 P. M.	8.71	293.8
	3.35 "	8.71	307.0

The pressure had become nearly constant. Some nitrogen was therefore admitted.

	3.38 P. M.	8.71	317.4
	4.20 "	8.71	313.0

Absorption was taking place very slowly. In order to see whether 313 or 305 was nearer the true value, nitrogen was pumped out.

	4.34 P. M.	8.71	309.0
	4.55 "	8.71	310.3

The results of this experiment are somewhat inconsistent, as the pressure was decreasing at 305 and increasing at 310 millimeters. The mean of these is 308 millimeters, and the mean temperature was 1297° C. The current in the lamp of the Wanner pyrometer was from 6.3 to 6.5 units.

Experiment 8.

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
June 14.	1.55 P. M.	9.86	444.0	5.80	1371°
	2.15 "	9.86	384.8
	2.45 "	9.69	373.8	5.83	1379
	3.15 "	9.73	375.3	5.88	1373
	3.45 "	9.73	375.4	5.82	1371
	4.45 "	9.65	376.1	5.80	1377
June 15.	8.45 A. M.	9.67
	9.15 "	9.71	374.2
	10.30 "	9.68	376.5	5.80	1380

The pressure had become constant. Nitrogen was therefore pumped out.

	11.13 A. M.	9.64	366.6
	11.30 "	9.65	370.2	5.88	1374
	12.30 P. M.	9.62	373.4
	1.30 "	9.65	377.3	5.84	1377
	4.30 "	9.55	379.3

It is seen that the pressure decreased until it became constant at about 376 millimeters, and after pumping out to 367 it increased to 379. The average mean is 378 millimeters, and the average temperature 1378° C.

The interior of the furnace after these runs was found covered with a thick white deposit.

The charge in the crucible gave tests in each case for carbide and calcium cyanamide. The latter was tested for by adding ammonia and silver nitrate, which, with cyanamide, give a yellow precipitate of silver cyanamide. The white powder taken from the walls of the furnace also gave the yellow precipitate on adding ammonia and silver nitrate to a solution of this substance.

Experiment 9.

In this run an attempt was made to measure an equilibrium at about 1440°. It was not successful, however, as will be seen from the following results.

Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
10.15 A. M.	10.60
10.20 "	10.88	650	5.75	1433
10.30 "	10.94	587
11.30 "	10.94	513
12.55 P. M.	10.94	514	5.80	1420
Some nitrogen pumped out.				
1.00 P. M.	10.94	458
1.15 "	10.94	468
2.00 "	10.94	469
Some nitrogen pumped out.				
2.05 P. M.	10.94	460
2.45 "	10.94	461
More nitrogen pumped out.				
2.50 P. M.	10.94	427
3.45 "	10.94	432.7	5.92	1448

It is evident that, though the reaction goes in both directions at this temperature, it is so slow that it is difficult to tell whether an equilibrium has been reached or not. The reason for this may have been that the charge had become very hard and could not be dug out of the crucible, and appeared as though it had been somewhat fused together. This would make it difficult for the nitrogen to penetrate its entire mass. The average temperature of this run was 1437°. A later attempt at 1448° was more successful, and is given in Experiment 15.

Experiment 10.

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature
June 21.	3.10 A. M.	5.58	222.2
	3.40 "	..	174.8	5.90	1171
	4.30 "	5.58	157.0	5.90	1165
	4.53 "	5.58	150.5
June 22.	8.30 "	5.62	149.2	5.80	1164
	10.30 "	5.72	144.0
	11.30 "	5.69	141.0	5.80	1172
	1.45 P. M.	5.69	133.8	5.82	1162
	4.00 "	5.56	127.6	5.80	1159
	4.45 "	5.64	125.8	5.82	..
June 23.	8.30 "	5.72	125.5	5.88	1159
	10.00 "	5.70	124.5	7.85	1155

The pressure had become constant. Some nitrogen was therefore pumped out to get the equilibrium from the other side.

Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
10.03 P. M.	5.69	102.2
12.30 "	5.71	104.2

The reaction went so slowly that it did not seem possible to get an equilibrium from this side at this temperature. The temperature was therefore raised.

1.00 P. M.	6.32	116.9	5.88	1199
2.00 "	6.31	142.0

The pressure was increasing rapidly, and in order not to use up all the calcium cyanamide, some nitrogen was admitted.

2.05 P. M.	6.27	160.0
2.30 "	6.30	160.4

Since the pressure remained constant, more nitrogen was admitted.

2.45 P. M.	6.30	189.7
3.00 "	6.31	181.0	5.87	1194
4.00 "	6.27	171.1	5.86	1193
4.45 "	..	168.1	5.90	1193
June 24. 8.30 A. M.	6.33	166.5
10.00 "	6.34	166.5

This value, 166.5 millimeters, seems to be the equilibrium. In order to get it from the other side some nitrogen was pumped out.

10.05 A. M.	6.29	152.6
10.30 "	6.30	155.0	5.87	1197
11.30 "	6.27	159.0	5.80	1198
1.00 P. M.	6.29	160.0	5.88	1193
3.00 "	6.32	159.6

The pressure increased to only 160 millimeters in place of 166. In order to see which was nearer the correct value, nitrogen was admitted.

3.03 P. M.	6.32	166.3
3.45 "	6.31	164.0	5.88	1199
4.55 "	6.28	162.4
June 25. 8.30 A. M.	0.00	123.0
9.00 "	6.34	162.8
10.30 "	6.33	162.9

In these last data the absorption took place to 162 millimeters. Combining this with the expansion to 160, the mean is 161 millimeters.

With the same charge the following data were then taken at a higher temperature, after admitting some nitrogen.

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
<i>June 27.</i>	9.00 A. M.	8.77	298.0
	9.45 "	7.50	280.9	5.90	1271
	11.50 "	7.53	274.6	5.80	1290
	12.45 P. M.	7.51	274.3

Here the pressure had nearly reached the equilibrium value, as it was decreasing very slowly. In order to get equilibrium from the other side, some nitrogen was pumped out.

	12.40 P. M.	7.51	257.6
	1.30 "	7.53	263.5	5.92	1280
	3.15 "	7.53	269.1	5.90	1280
	4.10 "	7.54	270.8	5.90	1280

The equilibrium therefore lies between 274 and 271, the mean of which is 273 millimeters. The mean temperature was 1278° C.

There was a great deal of white powder on the walls of the furnace after this long heating.

The following run was made using a heating spiral of twice the cross-section and half the length, heated by a direct current.

Experiment 11.

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
	9.00 A. M.	7.86	330.1	5.80	1360
	11.00 "	7.80	279.5	6.08	1310
	12.55 P. M.	7.77	282.4	6.01	1320
	2.00 "	7.71	282.8		

The equilibrium was approached only from one side, when the experiment was stopped on account of poor regulation of the temperature by this arrangement. The equilibrium found was 283 millimeters at a mean temperature of 1308° C.

Experiment 12.

The object of the following experiment was to measure an equilibrium between 1000° and 1100°. Since equilibrium could not be ob-

tained in both directions at 1160 without a catalyzer, calcium chloride was added to the charge for this experiment, to act as a catalyzer.⁴ The charge consisted of 22.5 grams of calcium carbide and 2.5 grams of dry calcium chloride, well mixed together.

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
<i>July 1.</i>	8.27 A. M.	4.07	151.8
	8.37 "	4.10	128.7	6.03	1050
	9.30 "	4.10	71.1
	10.30 "	4.08	44.9	6.00	1050
	12.45 P. M.	4.10	25.9
	2.00 "	4.08	24.2	6.12	1050
	2.30 "	4.08	23.7

Since the pressure had become fairly constant, some nitrogen was pumped out.

	2.35 P. M.	4.10	19.6
	4.45 "	4.07	21.8	6.10	1050

The constant pressure from the other direction is 22 millimeters.

The mean value at 1053° is 22.8 millimeters. With the same charge the following experiment was made at a higher temperature.

<i>July 5.</i>	11.30 A. M.	4.97	29.7
	12.15 "	4.99	50.8	6.09	1105
	1.45 "	4.99	56.3	5.98	1117
	3.00 "	4.99	57.7	6.10	1115

Here the pressure had become nearly constant, so nitrogen was admitted.

	3.15 P. M.	4.99	108.7
	4.50 "	4.98	78.5
<i>July 6.</i>	8.30 A. M.	4.97	74.4
	2.00 "	5.01	67.2	5.90	1115

Absorption was still taking place, but so slowly that the experiment was stopped. The mean of 67.2 and 57.7 is 62.5 millimeters at 1117° C.

Experiment 13.

The charge for this experiment was 22.5 grams of calcium carbide and 2.5 grams of calcium chloride.

⁴ That the chlorides of the alkali earth metals act in this way was discovered by Polzenius; see Bredig, *Z. f. Elektroch.*, **13**, 69 (1907).

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
<i>July 8.</i>	8.05 A. M.	0.	167.5	..	25
	8.10 "	4.96	199.7
	10.00 "	4.98	120.7

Some nitrogen pumped out, so as to reach equilibrium sooner.

	10.03 A. M.	5.02	108.0
	11.00 "	4.98	98.5

More nitrogen pumped out.

	11.05 A. M.	5.01	93.8
	2.00 P. M.	5.00	86.3	6.02	1110

More nitrogen pumped out.

	2.05 P. M.	5.01	83.2
	2.30 "	4.98	83.0

The pressure remained constant, and was then reduced to 73.4 and then to 70 and remained constant at both values. It was then reduced still more.

	4.02 P. M.	4.98	45.2
	4.50 "	4.98	48.0
<i>July 9.</i>	8.10 A. M.	5.00	35.3
	8.30 "	4.99	47.8
	9.45 "	5.00	50.9	6.05	1107
	10.00 "	..	51.1
	10.45 "	..	51.3

At a pressure of 86.3 millimeters, nitrogen was being slowly absorbed, and at 51.3 the pressure had become constant starting with a lower value. The mean of these is 68.3 millimeters, and the mean temperature was 1114°. No good reason why the velocity of the reaction was so slow in this case can be given.

Experiment 15.

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
<i>July 13.</i>	8.45 A. M.	0.	318.6
	8.50 "	10.9	415.
	9.30 "	10.9	428.5	6.1	1441
	10.00 "	10.9	429.5

It seemed that not enough nitrogen had been let into the furnace to start with, so more was admitted.

Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
10.22 A. M.	10.9	465.
11.00 "	10.9	449.0
11.30 "	10.9	448.0	6.1	1448

Absorption had taken place and the pressure had become constant. Nitrogen was then pumped out.

12.10 P. M.	10.9	430.5
12.30 "	10.9	433.5	6.1	1451
2.40 "	10.9	438.0

The pressure had become constant. Nitrogen was again admitted to see if the pressure would again diminish to 449.

2.43 P. M.	10.9	476.0
3.00 "	10.9	469.8
3.15 "	10.9	471.2	6.1	1445

It did not reach 449 but stopped at 470. On admitting more nitrogen, very little absorption took place, as seen below.

3.50 P. M.	10.9	496.3
4.15 "	10.9	495.7
4.30 "	10.9	494.5

This run may be summed up as follows: absorption took place from 465 to 449 millimeters, but when pumped out to 430.5 millimeters, the pressure increased to only 438 millimeters. After this the pressure remained constant at nearly any value. This may have been because the charge was changed by heating into a hard, solid mass, thus reducing the surface in contact with the nitrogen. This would explain why the reaction took place with a noticeable velocity only during the first part of the experiment.

The average of 449 and 438 is 444 millimeters, and the average temperature is 1448°C.

Experiment 16.

The charge in this experiment consisted of 21.5 grams of calcium carbide.

Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
Aug. 3. 11.31 A. M.	8.83	434
11.45 "	8.74	408	6.10	1353
12.30 P. M.	8.83	389
2.00 "	8.83	389	5.9-6.0	1379

The pressure had become constant, so nitrogen was pumped out.

Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
2.01 P. M.	8.74	373.3
2.20 "	8.70	379.9	6.00	1352
2.45 "	8.83	382.8	5.98	1368
3.30 "	8.85	384.2	5.9-6.0	1380
4.00 "	8.74	386.1	6.00	1361
4.30 "	8.70	386.0

The average temperature was 1372°C and pressures obtained from opposite directions were 386 and 389, the mean of which is 387.5 millimeters.

Experiment 17.

The charge consisted of 23.7 grams of carbide.

	Time.	Kilowatts.	Pressure.	Current in Wanner Pyrometer.	Temperature.
Aug. 5.	8.35 A. M.	00.00	328.1	..	25
	9.00 "	10.30
	9.05 "	10.30	423.0
	9.15 "	09.95	415.0
	11.05 "	09.95	381.0
	12.00 "	10.00	378.1	5.9	1396
	1.00 P. M.	10.20	379.0	5.9	1382
	1.45 "	10.20	379.7

The pressure had become constant, so nitrogen was pumped out.

	1.50 P. M.	10.2	354.9
	2.45 "	10.2	362.1	5.9	1387
	4.05 "	10.2	366.1	6.0	1385
	4.45 "	10.2	369.9	6.0	1390

The pressure was rising slowly when the experiment was stopped. The equilibrium is therefore nearer 380 than 370. However, the mean of these two, 375, is taken as the result of this run. The average temperature was 1385°C . The charge had become hard on the top but less so below the surface.

Experiment 18.

The disadvantage of the Arsem vacuum furnace for experiments of this kind is that the volume is so great that it takes quite a long time for the solid substance to absorb or evolve enough gas to reach equi-

librium pressure. It was therefore decided to try an experiment in the Heraeus furnace that had been used as an auxiliary furnace for calibrating the Wanner pyrometer. Of course this could be used only at comparatively low temperature. It was glazed only on the inside, and it was anticipated that it would leak.

The charge was contained in a graphite boat 1.5 inches long. It consisted of 6.14 grams of a mixture of calcium carbide and calcium chloride containing 10 per cent of the latter. The ends of the porcelain tube of the furnace were closed with rubber stoppers; the stoppers and ends of the tube were shellacked. A small glazed porcelain tube for holding the thermo-electric couple extended through the larger tube and the two stoppers. The junction was pushed in until it was opposite the graphite boat, in the middle of the furnace.

August 10th, at 5 P. M., the furnace was pumped out to a pressure of 1 millimeter and left till August 11th, 16 hours later, when it had leaked to 13.1 millimeters. The furnace was then heated to about 1070° and pumped out a number of times, after which the gases remaining were swept out with nitrogen. While still hot, nitrogen was admitted to 110 millimeters. Absorption was taking place rapidly, and the following observations were taken.

Time.	Pressure.	Temperature.
2 08 P. M.	110.0	..
2.10 "	32.0	1074
2.13 "	23.2	1074
2.20 "	21.5	1074
2.25 "	21.6	1074
2.32 "	22.1	1074
2.40 "	22.8	1077
2.45 "	23.2	1077

It seems that here the absorption of nitrogen at first overbalanced the leakage. The following day, minima of 26.8, 30, and 31.5 millimeters were obtained, starting with pressures of 145, 165, and between 100 and 200 millimeters respectively; and the best value of course would be obtained by starting very little above the equilibrium pressure, so that there would not be so much time for leakage to take place.

Although these determinations were somewhat in error from the leakage, this error was evidently not great, as the pressures agreed well with those obtained in the vacuum furnace. The temperature measurements were more reliable than the others, as they were made directly with the thermo-electric junction. The lowest pressure, 21.5

millimeters, is presumably the most reliable. The result of this run is therefore 21.5 millimeters at 1074° C.

The results of the above experiments are collected in the table below, and are plotted in Figure 5. The ordinates are pressures in centimeters of mercury and the abscissae are the temperatures in centigrade degrees. The pressures are not reduced to zero degrees as this correction is much less than the experimental error.

TABLE III.

Number of Experiment.	Pressure in Centimeters of Hg.	Temperature Centigrade.
4	27.0	1263
6	22.4	1223
7	30.8	1297
8	37.8	1378
10	12.5	1160
10	16.1	1196
10	27.3	1278
11	28.3	1308
12	2.3	1053
12	6.3	1117
13	6.8	1114
15	44.4	1448
16	38.8	1372
17	37.5	1385
18	2.2	1074

It is remarkable that the relation between the temperature and pressure is linear through such a great range in temperature. It would seem that at lower temperatures the line representing this relation must become concave upward, and it is hoped that in the near future it will be possible to carry out some experiments on this equilibrium below 1000 degrees, to test this point.

In order to compute the heat Q , evolved by the reaction $\text{CaC}_2 + \text{N}_2 \rightleftharpoons \text{CaCN}_2 + \text{C}$, taken from left to right, it is not allowable to use the integrated van't Hoff equation

$$4.57 \log \frac{p_2}{p_1} = Q \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

because this equation is derived on the assumption that Q is constant, which is not the case in this reaction. If Q is computed from the differential equation

$$\frac{dp}{dt} = \frac{Q}{T(V - V_1)},$$

in which T is the absolute temperature, V is the volume of the carbide and nitrogen and V_1 is that of calcium cyanamide and carbon on the other side of the equation, and $\frac{dp}{dt}$ is the pressure gradient at the tem-

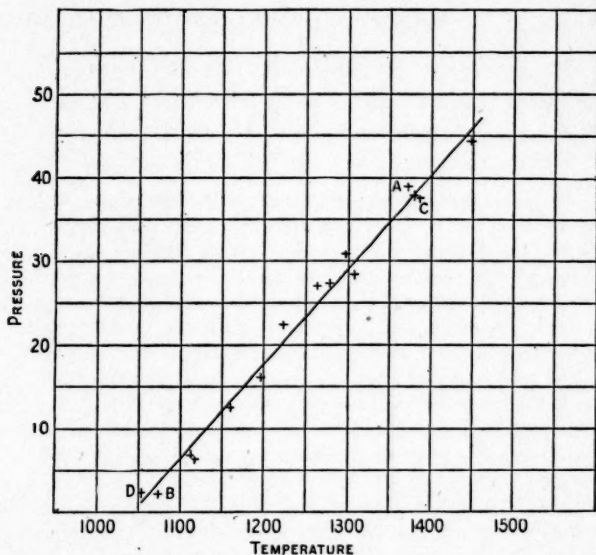


FIGURE 5. Plot showing pressures and temperatures at which equilibrium exists. Pressures are in centimeters of mercury; temperatures in centigrade degrees.

perature T , Q is found to have the values given in Table IV. The volume V_1 is negligible in comparison with V . Omitting V_1 the equation may be put in the following form:

$$Q = \frac{RT^2}{p} \frac{dp}{dt}.$$

The value of R is 1.99 calories, and the unit in which p is expressed cancels out.

TABLE IV.

SHOWING THE CHANGE IN THE HEAT OF THE REACTION WITH THE TEMPERATURE.

Temperature Centigrade.	Q in Gram Calories.
1100	63,900
1200	27,000
1300	18,800
1400	15,200

The value of $\frac{dp}{dt}$ is of course constant for every temperature.

The line as drawn in Figure 5 seems to represent the observations better than any other. The maximum variation in the slope would be represented by the lines *AB* and *CD*. From the value of $\frac{dp}{dt}$ obtained from these lines, the heat was calculated for 1200 degrees and found to be 29,700 and 25,800 calories respectively. This shows that the value calculated from the best representative line, 27,500, cannot be in error by more than 2000 calories, or 7 per cent.

It seems evident from the fact that the heat effect is greater the lower the temperature, that it would be advisable to work at as low a temperature as possible in the fixation of nitrogen by this method, because less heat would be required from external sources. This would be true if the velocity of the reaction did not decrease with decreasing temperature, for this might more than balance the benefit due to the increase in the heat of the reaction.

In view of the enormous increase in the heat of the reaction with decreasing temperature, as computed from these measurements, it is desirable that the heat should be measured in some other way. This might be done, as suggested by Mr. S. Peacock, by combustion experiments in a bomb. This would give indirectly the heat of the reaction at room temperature, which would be expected to be much larger than the values calculated above.

The free energy increase of the reaction



at 1450° C., taken from left to right is

$$\begin{aligned}\Delta F &= -RT \log \frac{1}{4} \\ &= -4.57 \times 1720 \times 0.218 \\ &= -1714 \text{ gram calories.}\end{aligned}$$

At 1100° C., $\Delta F = -6700$ calories.

The errors in the temperature measurements are probably the main cause of the deviations of the single determinations from the best representative line. If all the error is assumed due to the temperature measurements, the average deviation of a single point from the line is only 12 degrees, and the largest deviation is 19 degrees. These are not greater than the experimental errors in the temperature measurements.

The thermo-electric couple had been cut off several times since the original calibration. It was subsequently calibrated as follows :

TABLE V.

Date.	Temperature.	Millivolts at Date given.	Millivolts at Original Calibration.
July 2	Sulphur point	3.60	3.60
August 13	Copper point	10.08	10.19

The original calibration had therefore remained practically constant throughout the experiments.

After each experiment for determining the equilibrium pressure, the furnace walls were covered inside with a white powder. A similar result was obtained in determining the equilibrium of the reaction $\text{CaO} + 3\text{C} \rightleftharpoons \text{CaC}_2 + \text{CO}$.⁵ It was noticeable, however, that there was more powder formed with calcium cyanamide for a given temperature and given duration of heating than with calcium carbide. It seemed probable that calcium cyanamide is volatile, especially after it was found that the white powder gave a yellow precipitate of silver cyanamide on adding silver nitrate to an ammoniacal solution of the powder. It was therefore thought desirable to make an analysis of this material.

Some of the pure white powder was analyzed for nitrogen by the Kjeldahl method, taking about one gram for analysis. The digestion with chemically pure sulphuric acid was continued for five hours near the boiling point; immediately after, potassium permanganate was added. The two determinations gave 12.38 and 11.67 per cent nitrogen, corresponding to 34.3 per cent calcium cyanamide.

To get a check on this value, the calcium cyanamide was determined by the method of Perotti.⁶ This method consists in allowing the substance to stand over night in water, filtering and washing, adding ammonia, and then an excess of silver nitrate. A yellow precipitate of silver cyanamide is produced which is filtered off, and the

⁵ Trans. Am. Electroch. Soc., **15**, 197 (1909).

⁶ Chemisches Centralblatt, **2**, 1059 (1905).

excess of silver nitrate is titrated with ammonium sulphocyanate. The sample taken was not perfectly white, but from its gray color evidently contained some carbon which had also distilled to the wall of the furnace. The residue obtained on treating the white powder with water was of a dark grey color. It was evidently carbon and calcium oxide, for (1) it dissolved slightly in a fresh portion of water and gave a distinct precipitate when ammonia and ammonium oxalate were added; (2) on treating some that had been exposed to the air with hydrochloric acid it dissolved partly with effervescence, leaving a black residue behind; and (3) when the hydrochloric acid solution was neutralized with ammonia and ammonium oxalate was added, a large quantity of precipitate was formed. The analysis of the water solution for calcium cyanamide gave 38.59, 39.52, and 38.84 per cent corresponding to 13.51, 13.84, and 13.60 per cent nitrogen. An analysis of a sample of the same material used in the Kjeldahl determinations gave only 25.96 per cent calcium cyanamide, corresponding to 9.09 per cent nitrogen. Since this did not agree with the determinations by the Kjeldahl method or with the values obtained by the same method for other samples, analyses were made by the Perotti method of two more samples. The perfectly white material used in the Kjeldahl method could not be checked again as it had all been used up. The results of the analyses of the powder obtained in Experiment 16, were 15.96 and 15.35 per cent calcium cyanamide, corresponding to 5.59 and 5.38 per cent nitrogen. Analyses of the material obtained in Experiment 17 gave 29.10 and 28.95 per cent calcium cyanamide, corresponding to 10.19 and 10.13 per cent nitrogen. Experiments 16 and 17 were made at about the same temperature and still the amount of calcium cyanamide in the powder distilled to the cold part of the furnace was quite different.

Two determinations of calcium in the white powder used in the Kjeldahl determinations were made by first destroying the organic matter with fuming nitric acid and then decomposing the calcium nitrate by ignition in a platinum crucible and weighing as the oxide. The fuming nitric acid had to be added very slowly as it attacked the white powder with great violence, sometimes causing it to flame. The results were 39.93 and 39.27 per cent calcium, the average of which is 39.60 per cent. From this and the fact that the content of nitrogen was 12.1 per cent, the amounts of calcium oxide and of calcium cyanamide in the first sample of white powder analyzed were as follows:

Calcium cyanamide	34.5 per cent
Calcium oxide	30.5 " "
Unaccounted for	35.0 " "

Time did not permit of making a combustion analysis to see how the carbon checked up. This sample apparently contained very little free carbon, for it was of a cream white color.

Since calcium cyanamide was present in the powder distilled to the walls of the furnace, when heated with carbon it should produce calcium carbide with the evolution of nitrogen. In order to see whether this actually takes place, 0.4 gram of the powder was mixed with 0.9 gram Acheson graphite and heated in the vacuum furnace. The results are the following :

Experiment 14.

	Time.	Kilowatts.	Pressure.
July 11.	11.00 A. M.	0.	2.8
	11.12 "	0.33	10.
	11.20 "	0.78	..
	11.35 "	..	19.0
	11.35 "	1.27	..
	11.45 "	..	23.8
	11.45 "	1.8	..
	12.00 "	..	28.8
	12.00 "	2.7	..
	12.20 P. M.	..	67.
	12.20 "	5.3	..
	12.35 "	8.0	..
	12.45 "	..	183.
	2.15 "	..	195.

The temperature measured at 12.35 P.M., with the current in the Wanner 6.1 units, was 1287° C.

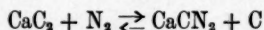
On opening the furnace after this run no white deposit was found on the walls, and the material in the crucible seemed to be hardly changed in appearance. It gave no test for carbide with an ammoniacal cuprous chloride solution, nor for cyanamide with silver nitrate. It is to be noticed, however, that a great deal more gas was evolved from this mixture on heating than on heating a sample of carbide, from which occluded gases always escape. For example, in Experiment 15, on heating carbide to 1450° C, these gases produced a pressure of 127 millimeters, which is considerably less than the 195 millimeters produced from the white powder and carbon at 1287°. It therefore seems certain that the large amount of gas evolved in Experiment 14 was due to a chemical reaction and not to occluded gases alone. A possible explanation of the absence of carbide in the crucible is that some oxygen got into the furnace. This

would be changed to carbon monoxide which would decompose any carbide formed. The result of the experiment is, however, not conclusive.

Since calcium oxide was found in the white powder, an experiment was carried out to see to what extent lime would distill when heated alone in a vacuum. A graphite crucible was filled with pieces of Merck's lime about the size of a pea, and was heated in a vacuum for three hours at 1531 degrees. On opening the furnace it was found covered on the inside with a thin greyish-white powder. On collecting this it filled about one half inch of an ordinary test tube, and was placed in a desiccator several days before testing. It was then dissolved in hydrochloric acid and tested for calcium with ammonia and ammonium oxalate; a large amount of precipitate of calcium oxalate was formed. This experiment therefore shows that lime distills at about 1500 degrees in a vacuum. This doubtless is the cause of the thin layers always found in the experiments on the equilibrium of the reaction $\text{CaO} + 3\text{C} \rightleftharpoons \text{CaC}_2 + \text{CO}$. It was not known at the time of the determination of this equilibrium that lime is distilled in the neighborhood of 1500 degrees.⁷

3. SUMMARY.

The equilibrium pressure of nitrogen in the reaction



was determined from both sides for a number of temperatures between 1050° C. and 1450° C. The results are plotted in Figure 5. It was found that the heat of the reaction varies enormously with the temperature. The values calculated from the plot in Figure 5 are given in Table IV.

The free energy increase of the reaction taken from left to right is -1714 gram calories at 1450° C. and -6700 calories at 1100° C.

Calcium cyanamide distills the cold parts of the vacuum furnace at temperatures as low as 1050° C. Pure lime distills appreciably in the neighborhood of 1500° C.

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BOSTON, MASS., September 23, 1910.

⁷ These Proceedings, 45, 449 (1910).

